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Modelling High Resolution Absorption Spectra with ExoMol Line Lists: NH_3 and CH_4

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Introduction

The conditions, chemical reactions and gas mixing in industrial progresses involving gasification or combustion can be monitored by *in situ* measurement of gas temperature and gas composition. This can be done spectroscopically, though the result is highly dependent on the quality of reference data [1].

For this reason, a *smart* collaboration has been established between Optical Diagnostics Group at DTU and ExoMol, to combine high resolution spectra measured at elevated temperatures and empirically tuned ab initio methods to produce suitable molecular line lists for modelling molecules in combustion or gasification processes.

Current Work

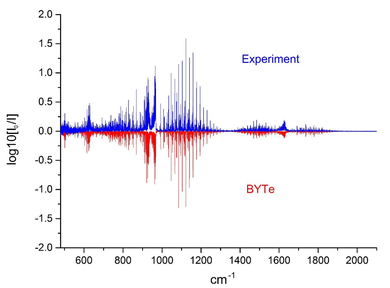
The current focus is on industrially important molecules NH_3 and CH_4 for which high temperature line lists, BYTe [2] and YT10to10 [3], are already available from ExoMol.

High-resolution absorption spectra (0.01 cm^{-1}) of NH_3 and a spectrum of CH_4 at temperatures up to 1027^0C and about atmospheric pressure have been measured. The measurements cover spectral regions 500 - 2100 cm^{-1} and 2100 - 5500 cm^{-1} for NH_3 and 1000 - 3500 cm^{-1} for CH_4.

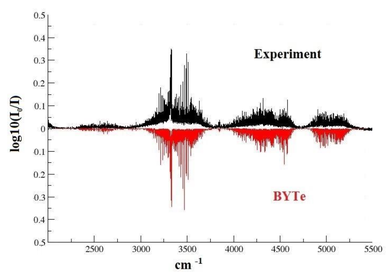
Experimental absorption spectra are compared to theoretical absorption spectra to assess the accuracy of the line lists and, where possible, assign experimental lines.

NH_3

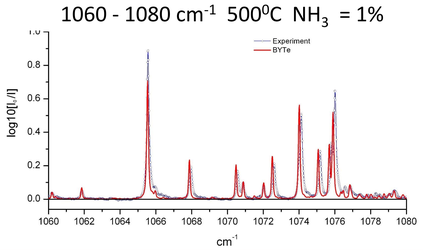
500 - 2100 cm^{-1} 500^0C NH_3 = 1%



2100 - 5500 cm^{-1} 1027^0C NH_3 = 10%



1060 - 1080 cm^{-1} 500^0C NH_3 = 1%



A comparison between the measurements and BYTe shows in general good agreement through there are some shifts in line position (up to 0.5cm^{-1}) and BYTe appears to be underestimating strong line intensities (by up to 30%).

Work towards a new NH_3 line list is currently be carried out as part of the ExoMol project [4], see poster by Philip Coles.

The high temperature NH_3 spectra in the region 500 - 2100 cm^{-1} has been analysed by comparison to BYTe and experimental energy levels determined using the MARVEL procedure [5]. The results have been accepted for publication in JQSRT [6].

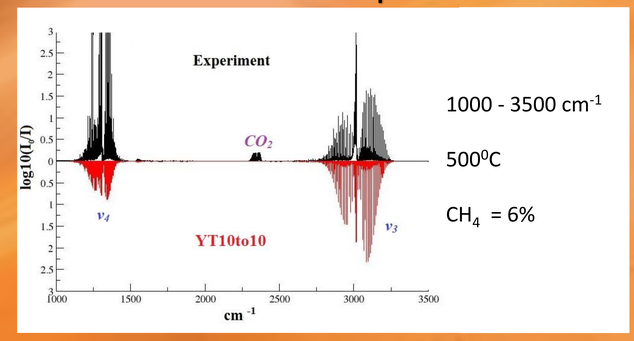
1967 lines have been assigned of which 1116 lines were previously assigned, 1073 by studies included in the HITRAN database and an additional 43 by high temperature study [7]. 851 lines have been assigned for the first time in this work, 482 were also present but unassigned in the spectra analysed by [7].

	Lines
Experiment	4309
HITRAN	1073
Zobov et al. [7]	43
New Trivial	326
New Line List	525
Total Assigned	1967

Lines were assigned to 54 different bands, 17 observed for the first time in this work, including bending hot bands up to $5\nu_2$. A summary of observed bands will be presented in the paper [6].

A new MARVEL analysis is underway. This *doesn't* necessarily affect the current work, though the updated energy levels could be used in conjunction with BYTe to analyse the higher region, 2100 – 5500 cm^{-1}.

CH_4



Two bands of CH_4 are present in the experimental spectrum, ν_4 (1200 – 1450 cm^{-1}) and ν_3 (2750 – 3250 cm^{-1}).

For ν_4, taking into account saturated lines in the experimental spectrum, YT10to10 reproduces experimental line positions and intensities within 0.5 cm^{-1} and 10% respectively.

For ν_3, taking into account the saturated Q-branch, YT10to10 reproduces experimental line positions within 0.3 cm^{-1}, but predicts intensities that are 30 – 40% higher than the observed ones.

Comparisons *with* more experimental spectra could help assess this issue.

Future Work

- Analyse the high temperature NH_3 absorption spectra in the region 2100 - 5500 cm^{-1} by comparison to BYTe and updated MARVEL energy levels.
- Obtain more spectral measurements for CH_4 over a wider spectral range and at higher temperatures.

References

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